

UK Patent Application GB 2 140 819 A

(43) Application published 5 Dec 1984

(21) Application No 8413673	(51) INT CL ³ C11D 3/386
(22) Date of filing 29 May 1984	(52) Domestic classification C5D 6A4B 6A5A 6B11A 6B12B1 6B12F2 6B12G2A 6B1 6B2 6B4 6B5 6B7 6B8 6C8
(30) Priority data (31) 499645 (32) 31 May 1983 (33) US	(56) Documents cited GB A 2079305
(71) Applicant Colgate-Palmolive Company (USA-Delaware), 300 Park Avenue, New York, New York 10022, United States of America	(58) Field of search C5D
(72) Inventors Jack Thomas Inamorato Michael Christopher Crossin	
(74) Agent and/or Address for Service Kilburn & Strode, 30 John Street, London WC1N 2DD	

(54) Built single-phase liquid anionic detergent composition containing stabilized enzymes

(57) A stabilized built single-phase enzyme-containing liquid detergent composition is provided comprising:

- (a) 8 to 20%, by weight, of a surface active anionic detergent compound;
- (b) 5 to 25% of a water-soluble non-phosphate detergent builder salt;
- (c) an effective amount of an enzyme or enzyme mixture selected from alkaline protease enzymes and alpha-amylase enzymes;
- (d) an enzyme stabilizing system containing, based on the weight of the detergent composition, (i) 12 to 25% of propylene glycol and (ii) 1 to 5% of a boron compound which is boric acid, boric oxide or an alkali metal borate, or a mixture thereof; and
- (e) 25 to 75% by weight of water.

GB 2 140 819 A

SPECIFICATION

Built single-phase liquid anionic detergent composition containing stabilized enzymes

5 The present invention relates to stable, built, enzyme-containing liquid detergent compositions suitable for laundry or pre-soak formulations. More particularly, the invention relates to aqueous enzyme-containing liquid detergent compositions which contain a non-phosphate detergent builder and which are characterised by being physically stable, clear, single-phase homogeneous liquid compositions. 5

10 The formulation of stabilized enzyme-containing liquid detergent compositions has been the focus of much attention in the prior art. The desirability of incorporating enzymes into detergent compositions is primarily due to the effectiveness of proteolytic and amylolytic enzymes in decomposing proteinaceous and starchy materials found on soiled fabrics, thereby facilitating the removal of stains, such as, gravy stains, blood stains, chocolate stains and the like during 10

15 laundering. However, enzymatic materials suitable for laundry compositions, particularly proteolytic enzymes, are relatively expensive. Indeed, they generally are the most expensive ingredient in a typical commercial liquid detergent composition, even when present in relatively minor amounts. Moreover, enzymes are known to be unstable in aqueous compositions. It is for this reason that an excess of enzymes is generally required in liquid detergent formulations to 15

20 compensate for the expected loss of enzyme activity during prolonged periods of storage. Accordingly, the prior art is replete with suggestions for stabilizing enzyme-containing liquid detergent compositions, and in particular unbuilt liquid compositions by the use of various materials which are incorporated into the composition and serve as enzyme stabilizers. 20

In the case of liquid detergent compositions containing a builder, the problem of enzyme 25 instability is particularly acute. Primarily this is because detergent builders have a destabilizing effect on enzymes, even in compositions containing enzyme stabilizers which are otherwise effective in unbuilt formulations. Moreover, the incorporation of a builder into a liquid detergent composition poses an additional problem, namely, the ability to form a stable single-phase solution, the solubility of sodium tripolyphosphate, for example, being relatively limited in 25

30 aqueous compositions, and especially in the presence of anionic and nonionic detergents. Thus, for example, in U.K. Patent Application G.B. 2,079,305, published 20th January, 1982, there is disclosed an aqueous built enzyme-containing liquid detergent composition which is stabilized by a mixture of a polyol and boric acid. The compositions described in the examples, however, rather than being stable, clear, single-phase solutions, are instead turbid suspensions which are 30

35 susceptible to product separation over prolonged periods of storage. Consequently, the problems of enzyme stability and physical product stability remain as problems yet to be overcome in formulating a commercially acceptable built enzyme-containing liquid detergent composition. 35

The present invention provides a stabilized aqueous, built, clear, single-phase, enzyme-containing liquid detergent composition comprising: 40

40 (a) from about 8 to 20%, by weight, of one or more surface active anionic detergent compounds;

(b) from about 5 to 25%, by weight, of a water-soluble non-phosphate detergent builder salt;

(c) an effective amount of an enzyme or enzyme mixture comprising alkaline protease enzymes and alpha-amylase enzymes;

45 (d) an enzyme stabilizing system containing, based on the weight of the detergent composition (i) from about 12 to 25% of propylene glycol and (ii) from about 1 to 5% of a boron compound consisting of boric acid, boric oxide or an alkali metal borate or mixtures thereof; and

(e) from about 25 to 75% by weight of water.

In accordance with the process of the present invention, laundering of stained and/or soiled 50 materials is effected by contacting such materials with an aqueous solution of the above-defined liquid detergent composition. Unlike the built, enzyme-containing detergent compositions known in the art, the compositions of the present invention are characteristically clear, single-phase homogeneous solutions which are physically stable over prolonged periods of storage and over a wide range of temperature. To avoid product separation, the present compositions are preferably 50

55 substantially free of phosphate builder salt.

Unlike the enzyme-containing built liquid anionic detergent compositions disclosed in the art, the anionic surfactant in the compositions of the present invention is solubilized in the presence of a builder salt. Moreover, the present enzyme-containing compositions are characterised by the presence of an enzyme-stabilizing system which in addition to providing long-term stability to 60 the enzyme over a wide range of temperatures, serves to enhance the solubility of the anionic surfactant and the non-phosphate builder in the aqueous composition allowing a physically stable single-phase solution to be formed for the particular range of compositions indicated. 60

The enzyme stabilizing system of the present invention is a mixture of propylene glycol and a boron compound selected from among boric acid, boric oxide and alkali metal borate capable of 65 reacting with propylene glycol. The amount of propylene glycol is from about 12 to 25%, 65

preferably from about 15 to 20%, by weight, and the amount of the boron compound is from about 1 to 5%, preferably from about 1 to 3%, by weight of the composition.

The alkaline proteolytic enzymes suitable for the compositions of the present invention include the various commercial liquid enzyme preparations which have been adapted for use in

5 detergent compositions, enzyme preparations in powdered form being also useful although, as a general rule, less convenient for incorporation into the built liquid detergent compositions. Thus, suitable liquid enzyme preparations include "Alcalase" and "Esperase" sold by Novo Industries, Copenhagen, Denmark, and "Maxatase" and "AZ-Protease" sold by Gist-Brocades, Delft, The Netherlands. Esperase is particularly preferred for the present composition because of its
10 optimized activity at the higher pH values corresponding to built detergent compositions. 10

Among the suitable α -amylase liquid enzyme preparations are those sold by Novo Industries and Gist-Brocades under the tradenames "Termamyl" and "Maxamyl", respectively.

The synthetic anionic detergent employed in the practice of the present invention may be any of wide variety of such compounds which are well known and are described at length in the text

15 15 Surface Active Agents, Vol. II, by Schwartz, Perry and Berch, published in 1958 by Interscience Publishers, the disclosures pertaining to such detergent being hereby incorporated by reference.

The most preferred anionic detergent compounds are the higher (10 to 18 or 20 carbon atoms) alkyl benzene sulphonate salts wherein the alkyl group preferably contains 10 to 15 carbon atoms, most preferably being a straight chain alkyl radical of 12 to 13 carbon atoms.

20 Preferably, such an alkyl benzene sulphonate has a high content of 3- (or higher) phenyl isomers and a correspondingly low content (usually well below 50%) of 2- (or lower) phenyl isomers; in other words, the benzene ring is preferably attached in large part at the 3, 4, 5, 6 or 7 position of the alkyl group and the content of isomers in which the benzene ring is attached at the 1 or 2 position is correspondingly low. Typical alkyl benzene sulphonate surface active agents are
25 described in U.S. Patent 3,320,174. Of course, more highly branched alkyl benzene sulphonates may also be employed but usually are not preferred, due to their lack of biodegradability. 25

Other anionic detergents which are useful are the olefin sulphonate salts. Generally, these contain long chain alkenyl sulphonates or long chain hydroxyalkane sulphonates (with the OH being on the carbon atom which is not directly attached to the carbon atom bearing the $-SO_3H$ group). The olefin sulphonate detergent usually comprises a mixture of such types of compounds in varying amounts, often together with long chain disulphonates or sulphate-sulphonates. Such olefin sulphonates are described in patents, such as U.S. Patent Nos. 2,061,618; 3,409,637; 3,332,880; 3,420,875; 3,428,654; 3,506,580; and British Patent No. 1,129,158. The number of carbon atoms in the olefin sulphonate is usually within the range of 30 10 to 25, more commonly 10 to 18 or 20, e.g. a mixture principally of C_{12} , C_{14} and C_{16} , having an average of about 14 carbon atoms, or a mixture principally of C_{14} , C_{16} and C_{18} , having an average of about 16 carbon atoms. 35

Another class of useful anionic detergents is that of the higher paraffin sulphonates. These may be primary paraffin sulphonates made by reacting long chain alpha-olefins and bisulphites, 40 e.g. sodium bisulphite, or paraffin sulphonates having the sulphonate groups distributed along the paraffin chain, such as the products made by reacting a long chain paraffin with sulphur dioxide and oxygen under ultraviolet light, followed by neutralization with sodium hydroxide or other suitable base (as in U.S. Patents 2,503,280; 2,507,088; 3,260,741; 3,372,188; and German Patent 735,096). The paraffin sulphonates preferably contain from 13 to 17 carbon atoms and will normally be the monosulphonate but if desired, may be di-, tri- or higher sulphonates. Typically, the di- and polysulphonates will be employed in admixture with a corresponding monosulphonate, for example, as a mixture of mono- and disulphonates containing up to about 30% of the disulphonate. The hydrocarbon substituent thereof is preferably linear but if desired, branched chain paraffin sulphonates can be employed, although they are 45 inferior with respect to biodegradability. 50

Other suitable anionic detergents are sulphated ethoxylated higher fatty alcohols of the formula $RO(C_2H_4O)_mSO_3M$, wherein R represents a fatty alkyl group of from 10 to 18 or 20 carbon atoms, m is from 2 to 6 or 8 (preferably having a value from about 1/5 to 1/2 the number of carbon atoms in R) and M is a solubilizing salt-forming cation, such as an alkali metal, ammonium, lower alkylamino or lower alkanol-amino, or a higher alkyl benzene sulphonate wherein the higher alkyl group is of 10 to 15 carbon atoms. 55

Ethylene oxide is the preferred lower alkylene oxide of the anionic alkoxylate detergent, and the proportion thereof in the polyethoxylated higher alkanol sulphate is preferably 2 to 5 moles of ethylene oxide groups present per mole of anionic detergent, with three moles being most preferred, especially when the higher alkanol is of 11 or 12 to 15 carbon atoms. To maintain the desired hydrophilelipophile balance, when the carbon atom content of the alkyl chain is in the lower portion of the 10 to 18 carbon atom range, the ethylene oxide content of the detergent may be reduced to about two moles per mole whereas when the higher alkanol is of 16 to 18 carbon atoms in the higher part of the range, the number of ethylene oxide groups 60 65 may be increased to 4 or 5 and in some cases to as high as 8 or 9. Similarly, the salt-forming

cation may be varied to obtain the best solubility. It may be any suitably solubilizing metal or radical but will most frequently be alkali metal, e.g. sodium, or ammonium. If lower alkylamine or alkanolamine groups are utilized the alkyl groups and alkanols will usually contain from 1 to 4 carbon atoms and the amines and alkanolamines may be mono-, di- and tri-substituted, as in 5 monoethanolamine, diisopropanolamine and trimethylamine.

The poly-lower alkoxy higher alkanol sulphates may be employed in combination with other preferred anionic detergents such as the higher alkyl benzene sulphonates to provide optimum detergency in the present built liquid detergent compositions. A preferred polyethoxylated alcohol sulphate detergent is available from Shell Chemical Company and is marketed as Neodol 10 (Registered Trade Mark) 25-3S.

Examples of the higher alcohol polyethenoxy sulphates which may be employed in the liquid detergent compositions of the invention include: mixed C_{12-15} normal or primary alkyl triethenoxy sulphate, sodium salt; myristyl triethenoxy sulphate, potassium salt; n-decyl diethenoxy sulphate, diethanolamine salt; lauryl diethenoxy sulphate, ammonium salt; palmityl tetraethenoxy sulphate, sodium salt; mixed C_{14-15} normal primary alkyl mixed tri- and tetra-ethenoxy sulphate, sodium salt; stearyl pentaethenoxy sulphate, trimethylamine salt; and mixed C_{10-18} normal primary alkyl triethenoxy sulphate, potassium salt.

Other useful anionic detergents include the higher acyl sarcosinates, e.g. sodium N-lauroyl sarcosinate; higher fatty alcohol sulphates, such as sodium lauryl sulphate and sodium tallow 20 alcohol sulphate; sulphated oils; sulphates of mono- or di-glycerides of higher fatty acids, e.g. stearic mono-glyceride monosulphate; although, of these, the sodium higher alcohol sulphates have been found to be inferior to the polyethoxylated sulphates in detergency; aromatic poly(lower alkenoxy) ether sulphates, such as the sulphates of the condensation products of ethylene oxide and nonyl phenol (usually having 1 to 20 oxyethylene groups per molecule, 25 preferably 2 to 12); polyethoxy higher alcohol sulphates and alkyl phenol polyethoxy sulphates having a lower alkoxy (of 1 to 4 carbon atoms, e.g. methoxy) substituent on a carbon close to that carrying the sulphate group, such as monomethyl ether monosulphate of a long chain vicinal glycol, e.g. mixture of vicinal alkane diols of 16 to 20 carbon atoms in a straight chain; acyl esters of isethionic acid, e.g. oleyl taurides; higher alkyl phenyl polyethoxy sulphonates; 30 higher alkyl phenyl polyethoxy sulphonates; higher alkyl phenyl di-sulphonates, e.g. pentadecyl phenyl disulphonate; and higher fatty acid soaps, e.g. mixed coconut oil and tallow soaps in a 1:4 ratio.

Among the aforementioned types of anionic detergents, the sulphates and sulphonates are generally preferred but the corresponding organic phosphates and phosphonates may also be 35 employed when their contents of phosphates are not objectionable. Generally, the water soluble anionic synthetic organic detergents, (including soaps), are salts of alkali metal cations, such as potassium, lithium, and especially sodium, although salts of ammonium and substituted ammonium cations, such as those previously described, e.g. triethanolamine, triisopropylamine, may also be used.

40 A nonionic detergent may optionally be employed in minor amounts to supplement the anionic detergent compound in the built liquid detergent compositions of the present invention. When used in such combination with an anionic detergent, the amount of nonionic detergent will generally be below about 10%, and preferably below about 5%, by weight, of the total composition.

45 The nonionic detergents are usually poly-lower alkoxylated lipophiles wherein the desired hydrophile-lipophile balance is obtained from addition of a hydrophilic poly-lower alkoxy group to a lipophilic moiety. For the compositions of the present invention the nonionic detergent employed is preferably a poly-lower alkoxylated higher alkanol wherein the alkanol is of 10 to 18 carbon atoms and wherein the number of moles of lower alkylene oxide (of 2 or 3 carbon 50 atoms) is from 3 to 12. Of such materials it is preferred to employ those wherein the higher alkanol is a higher fatty alcohol of 11 or 12 to 15 carbon atoms and which contain from 5 to 8 or 9 lower alkoxy groups per mole. Preferably, the lower alkoxy group is an ethoxy group but in some instances it may be desirably mixed with propoxy groups, the latter, if present, usually being a minor (less than 50%) constituent. Exemplary of such compounds are those wherein the 55 alkanol is of 12 to 15 carbon atoms and which contain about 7 ethylene oxide groups per mole, e.g. Neodol (Registered Trade Mark) 25-7 and Neodol 23-6.5 which products are made by Shell Chemical Company, Inc. The former is a condensation product of a mixture of higher fatty alcohols averaging about 12 to 15 carbon atoms, with about 7 moles of ethylene oxide and the latter is a corresponding mixture wherein the carbon atoms content of the higher fatty alcohol is 60 12 to 13 and the number of ethylene oxide groups per mole averages about 6.5. The higher alcohols are primary alkanols. Other examples of such detergents include Tergitol (Registered Trade Mark) 15-S-7 and Tergitol 15-S-9, both of which are linear secondary alcohol ethoxylates made by Union Carbide Corporation. The former is a mixed ethoxylation product of an 11 to 15 carbon atom linear secondary alkanol with seven moles of ethylene oxide and the latter is a similar product but with nine moles of ethylene oxide being reacted.

65

Also useful in the present compositions are higher molecular weight nonionics, such as Neodol 45-11, which are similar ethylene oxide condensation products of higher fatty alcohols, with the higher fatty alcohol being of 14 to 15 carbon atoms and the number of ethylene oxide groups per mole being about 11. Such products are also made by Shell Chemical Company.

5 Other useful nonionics are represented by Plurafac B-26 (BASF Chemical Company), the reaction product of a higher linear alcohol and a mixture of ethylene and propylene oxides. 5

In the preferred poly-lower alkoxylated higher alkanols, the best balance of hydrophilic and lipophilic moieties are obtained when the number of lower alkoxy groups are from about 40% to 100% of the number of carbon atoms in the higher alcohol, preferably 40 to 60% thereof. The 10 nonionic detergent is preferably comprised of at least 50% of the preferred ethoxylated alkanols. 10 Higher molecular weight alkanols and various other normally solid nonionic detergent compounds and surfactants may contribute to gelation of the liquid detergent composition and consequently, are normally omitted or limited in quantity in the compositions of the present invention, although minor proportions thereof may be employed for their cleaning properties, 15 etc. With respect to both preferred and less preferred nonionic detergents, the alkyl groups present therein are preferably linear although minor degrees of slight branching may be tolerated, such as at a carbon next to or two carbons removed from the terminal carbon of the straight chain and away from the ethoxy chain with the proviso that such branched alkyl group is no more than three carbon atoms in length. Normally the proportion of carbon atoms in such 20 a branched configuration will be minor, rarely exceeding 20% of the total carbon atom content of the alkyl group. Similarly, although linear alkyl groups which are terminally joined to the ethylene oxide chains are highly preferred and are considered to result in the optimum combination of detergency, biodegradability and non-gelling characteristics, medial or secondary joiner to the ethylene oxide in the chain may occur. In such instance, it is usually in only a 25 minor proportion of such alkyl groups, generally less than 20% but as is in the case of the aforementioned Tergitols, may be greater. Also, when propylene oxide is present in the lower alkylene oxide chain, it will usually be less than 20% thereof and preferably less than 10% thereof.

The non-phosphate detergent builder salts are employed in the present compositions in 30 amounts of from about 5 to 25%, and preferably from about 1 to 20%, by weight. Specific examples of non-phosphorous water-soluble inorganic builders include water-soluble inorganic carbonate, bicarbonate and silicate salts. The alkali metal, for example, sodium and potassium, carbonates, bicarbonates and silicates are particularly useful herein. 30

Water-soluble organic builders are also useful and include the alkali metal, ammonium and 35 substituted ammonium polyacetates, carboxylates, polycarboxylates and polyhydroxysulphonates. Specific examples of polyacetate and polycarboxylate builders include sodium, potassium, lithium, ammonium and substituted ammonium salts of ethylene diaminetetracetic acid, nitrilotriacetic acid, benzene polycarboxylic (i.e. penta- and tetra-) acids, carboxymethoxysuccinic acid and citric acid.

40 The percentage of water, the main solvent in the present compositions, will usually be from about 25 to 75%, preferably 40 to 60%, by weight, of the liquid composition. 40

The optical fluorescent brighteners or whiteners usually employed in liquid detergent compositions are important constituents of modern detergent compositions which give washed laundry and materials a bright appearance so that the laundry is not only clean but also appears 45 clean. Although it is possible to utilize a single brightener for a specific intended purpose in the liquid detergent compositions of the present invention it is generally desirable to employ mixtures of brighteners which will have good brightening effects on cotton, nylons, polyesters and blends of such materials and which are also bleach stable. A good description of such types of optical brighteners is given in the article "The Requirements of Present Day Detergent 50 Fluorescent Whiteners Agents" by A.E. Siegrist, J. Am. Oil Chemists Soc., January 1978 (Vol. 55). That article and U.S. Patent 3,812,041, issued 21st May, 1974, both of which are hereby incorporated by reference contain detailed descriptions of a wide variety of suitable optical brighteners.

Among the brighteners that are useful in the present liquid detergent compositions are: 55 Calcofluor 5BM (American Cyanamid); Calcofluor White ALF (American Cyanamid); SOF A-2001 (Ciba); CDW (Hilton-Davis); Phorwite RKH, Phorwite BBH and Phorwite BHC (Verona); CSL, powder, acid (American Cyanamid); FB 766 (Verona); Blancophor PD (GAF); UNPA (Geigy); Tinopal RBS 200 (Geigy).

60 Adjuvants may be present in the liquid detergent compositions to provide additional properties, either functional or aesthetic. Included among the useful adjuvants are soil suspending or antiredeposition agents, such as polyvinyl alcohol, sodium carboxymethyl cellulose, hydroxypropylmethyl cellulose; thickeners, e.g. gums, alginates, agar agar; foam improvers, e.g. lauric myristic diethanolamide; foam destroyers, e.g. silicones; bactericides, e.g. tribromosalicylanilide and hexachlorophene; dyes; pigments (water dispersible); preservatives; ultra-violet absorbers; fabric softeners; opacifying agents, e.g. polystyrene suspensions; 65

and perfumes. Of course, such materials will be selected based on the properties desired in the finished product, their compatibility with the other constituents, and their solubility in the liquid composition.

The present liquid compositions are efficient and easy to use. Compared to heavy duty laundry detergent powders, much smaller volumes of the present liquids may be employed to obtain comparable cleaning of soiled laundry. For example, using a typical preferred formulation of the present invention, only about 132 grams or 1/2 cup of liquid is needed for a full tub of wash in a top-loading automatic washing machine in which the water volume is 15 to 18 gallons (55 to 75 litres); and even less is needed for front-loading machines. Thus, the concentration of the liquid detergent composition in the wash water is on the order of about 0.2%. Usually, the proportion of the liquid composition in the wash solution will range from about 0.05 to 0.3%, preferably from 0.15 to 0.25%. The proportions of the various constituents of the liquid composition may vary accordingly. Equivalent results can be obtained by using greater proportions of a more dilute formulation but the greater quantity needed will require additional packaging and will generally be less convenient for consumer use.

The invention may be put into practice in various ways and a number of specific embodiments will be described to illustrate the invention with reference to the accompanying examples.

EXAMPLES 1A to 1E

Enzyme-containing built liquid detergent compositions were formulated as set forth in Table 1. The values shown indicate weight percent. Examples 1A and 1B are comparison examples.

TABLE 1

Example	1A	1B	1C	1D	1E	
<i>Ingredient</i>						
Sodium dodecylbenzene sulphonate	7	7	7	7	7	
Ethoxylated C ₁₂ –C ₁₅ alcohol sulphate (3 mole EO/mole alcohol) ⁽¹⁾	7	7	7	7	7	30
Brightener	0.2	0.2	0.2	0.2	0.2	
Sodium Nitrilotriacetate	15	15	15	15	15	
PBB ⁽²⁾	1	1	1	1	1	35
Perfume	0.3	0.3	0.3	0.3	0.3	
Protease enzyme ⁽³⁾	1	1	1	1	1	
Propylene glycol	—	20	20	20	20	
Borax	—	—	1	2	3	
Water			balance			40
Percent active enzyme after						
(a) 4 days at 110°F (43°C)	—	—	—	—	98%	
(b) 6 days at 110°F (43°C)	0	15	61	86	88	45

Notes on Table 1:

(1) Neodol 25-3S sold by Shell Oil Company.
 (2) Polar Brilliant Blue – a 1% active dye solution.
 (3) "Esperase" sold by Novo Industries containing 5% enzyme, 75% propylene glycol, and balance water having an activity of 8.0 KNPU/gm. (Kilo Novo Protease units/gm).

The enzyme activities of the compositions of Examples 1A to 1E were tested after 6 days storage at 110°F (43°C), the percent activity relative to the initial value being indicated in Table 1. The activity after 4 days was measured only for the composition of Example 1C. The compositions of Examples 1A and 1B were the only compositions which did not contain an enzyme stabilizing system in accordance with the present invention, and manifested a total (Example 1A) or near total (Example 1B) loss of enzyme activity after 6 days. The compositions of Examples 1C, 1D and 1E reflect the marked improvement of enzyme stability attendant on the inclusion of propylene glycol and borax in the detergent composition.

The compositions of Examples 1B to 1E were all clear, single-phase, homogeneous solutions which maintained their physical stability and clarity after 6 months of storage at both room temperature and at 110°F (43°C). The composition of Example 1A which was not in accordance with the invention was physically unstable due to the absence of propylene glycol which in

addition to serving as an enzyme stabilizer (in conjunction with the aforementioned boron compound) promotes the solubility of the anionic detergents and the NTA builder in the aqueous composition.

5 **EXAMPLES 2A and 2B**

Example 2A is a comparison example. Enzyme-containing built liquid detergent compositions (Examples 2A and 2B) were formulated essentially similarly to the compositions of Examples 1A to 1E except that sodium citrate was used as the builder salt instead of sodium NTA. The ingredients are shown below in Table 2, and the amounts are weight percentages.

10

5

TABLE 2

Example	2A	2B	
15 <i>Ingredient</i>			15
Sodium dodecyl benzene sulphonate	7	7	
Ethoxylated C ₁₂ -C ₁₅ alcohol sulphate (3 moles EO/mole alcohol)	7	7	
Brightener	0.2	0.2	
20 Sodium citrate	12	12	20
PBB ⁽¹⁾	1	1	
Perfume	0.3	0.3	
Protease enzyme ⁽²⁾	1	1	
Propylene glycol	20	20	
25 Borax	—	2	25
Water	balance		
Percent active enzyme after 4 days at 110°F (43°C)	20	95	
30			30

Notes of Table 2:

(1) Polar Brilliant Blue—a 1% active dye solution.
 35 (2) "Eperase" sold by Novo Industries containing
5% enzyme, 75% propylene glycol, and balance
water having an activity of 8.0 KNPU/gm. (Kilo
Novo Protease units/gm).

40 The composition of Example 2B in accordance with
the present invention manifested an enzyme activity
after four days of 95% as compared to the compo-
sition of Example 2A which contained no boron
compound and consequently lost more than 75% of
45 its initial enzyme activity.

Both compositions were clear single-phase solutions
which remained physically stable after six months of
storage at both room temperature and 110°F (43°C).

50 **EXAMPLES 3A to 3C**
 Example 3A is a comparison Example. Enzyme-
containing built liquid detergent compositions
(Examples 3A to 3C) were formulated essentially
similarly to the compositions of Example 2 except
 55 that they contained a mixture of protease and alpha-
amylase enzymes instead of a single protease en-
zyme. The ingredients are shown in Table 3 and the
amounts are in weight percent.

TABLE 3

Example	3A	3B	3C	
5				5
Ingredient				
Sodium dodecyl benzene sulphonate	7	7	7	
Ethoxylated C ₁₂ -C ₁₅ alcohol sulphate (3 moles EO/mole alcohol)	7	7	7	10
Brightener	0.2	0.2	0.2	
Sodium citrate	12	12	12	
PBB ⁽¹⁾	1	1	1	
Perfume	0.3	0.3	0.3	
15 Protease enzyme ⁽²⁾	1	1	1	15
α-Amylase enzyme ⁽³⁾	0.4	0.4	0.4	
Propylene glycol	20	20	20	
Borax	—	1	3	
Water		balance		
20				20
Percent active enzyme after 4 days at 100°F (43°C)				
α-amylase enzyme	50%	67%	87%	
Protease enzyme	30	73	94	
25				25

Notes on Table 3:

(1) Polar Brilliant Blue—a 1% active dye solution.

30 (2) "Eperase" sold by Novo Industries containing 5% enzyme, 75% propylene glycol, and balance water having an activity of 8.0 KNPU/gm. (Kilo Novo Protease units/gm). 30

(3) "Termamyl" sold by Novo Industries containing 5% enzyme, 18% sodium chloride and balance water having an activity of 120,000 Novo amylase units per gram.

35 The compositions of Examples 3B and 3C in accordance with the present invention demonstrated a markedly more stable enzyme activity after four days for both the protease and amylase enzymes relative to the composition of Example 3A which contained no boron compound and consequently lost about 50% of its initial amylolytic activity and about 33% of its initial proteolytic activity during the period of four days. 35

40 All three compositions were clear single-phase solutions which remained physically stable after six months of storage. 40

CLAIMS

1. A stabilized aqueous, built, clear, single-phase, enzyme-containing liquid detergent composition comprising:
 - from about 8 to 20%, by weight, of one or more surface active anionic detergent compounds;
 - from about 5 to 25%, by weight, of a water-soluble non-phosphate detergent builder salt;
 - an effective amount of an enzyme or enzyme mixture selected from the group consisting of alkaline protease enzymes and alpha-amylase enzymes;
 - an enzyme stabilizing system containing, based on the weight of the detergent composition, (i) from about 12 to 25% of propylene glycol and (ii) from about 1 to 5% of a boron compound consisting of boric acid, boric oxide or an alkali metal borate or mixtures thereof; and
 - from about 25 to 75% by weight of water.
2. A detergent composition as claimed in Claim 1 in which the said builder salt comprises sodium citrate.
3. A detergent composition as claimed in Claim 1 or Claim 2 in which the said builder salt comprises sodium nitrilotriacetate.
4. A detergent composition as claimed in Claim 1, 2 or 3 which is substantially free of a phosphate detergent builder salt.
5. A detergent composition as claimed in any one of Claims 1 to 4 which contains from about 15 to 20%, by weight, of propylene glycol and from about 1 to 3%, by weight, of the said boron compound.
6. A detergent composition as claimed in any one of Claims 1 to 5 in which the said boron

compound comprises borax.

7. A detergent composition as claimed in any one of Claims 1 to 6 in which the said builder salt is present in an amount of from about 10 to 20%, by weight.

8. A detergent composition as claimed in any one of Claims 1 to 7 in which the anionic detergent is a mixture of a C₁₀-C₁₈ alkyl benzene sulphonate salt and a polyethoxylated C₁₀-C₁₈ alcohol sulphate salt. 5

9. A detergent composition as claimed in Claim 1 substantially as specifically described herein with reference to Example 1C, 1D or 1E, 2B or 2C or 3B or 3C.

10. A method of laundering comprising contacting the stained and/or soiled fabrics to be laundered with an enzyme-containing, built, clear single-phase liquid detergent composition as 10 claimed in any one of Claims 1 to 9.

Printed in the United Kingdom for Her Majesty's Stationery Office, Dd 8818935, 1984, 4235.
Published at The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.